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(54) **Producing printed circuits by soldering metal powder images.**

(57) By the process of this invention, printed circuits are prepared containing an electrically conductive wiring trace from materials having adherent and non-adherent surface areas, e.g., printed circuit substrates bearing an imaged photoadhesive layer. Onto the adherent surface areas of the material is applied solder wettable metal particles, and any excess particles are removed from the non-adherent areas. The metallized areas are soldered to form an electrically conductive wiring trace.

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Croydon Printing Company Ltd.

PD 1597

Title

Producing Printed Circuits By Soldering Metal Powder Images

Description

Technical Field

This invention relates to a new additive method for preparing printed circuits including multilayer printed circuits, and pertains more particularly to the preparation of printed circuits by soldering metallized areas. This invention also relates to new printed circuit elements.

Background Art

Powdered materials such as metal particles have been applied to surfaces having imagewise tacky and non-tacky areas by a number of toning methods to produce printed circuit patterns. Representative methods are disclosed in U. S. Patents 3,060,024; 3,391,455; 3,506,483; 3,637,385; 3,649,268; 4,054,479; and 4,054,483. After the metal particles are applied to the tacky image areas and unwanted particles are removed, e.g., mechanically, from the non-tacky image areas, the circuit is formed by one of several additive techniques including fusion of metal particles, electroless plating, electroplating, etc. The printed circuits formed by these additive processes are useful, but the processes have certain disadvantages. For

example they are time consuming, costly, require high temperatures or pH and skillful operators, and are difficult to automate. It is also difficult by some of these processes to prepare certain printed circuits, particularly circuits having a fine conductive wiring trace. The above disadvantages have been overcome by a process whereby printed circuits containing electrically conductive circuit traces can be produced almost instantly and in an automated procedure without costly and lengthy treatment such as electroless plating.

Disclosure of Invention

In accordance with this invention, a printed circuit containing an electrically conductive circuit trace is produced from a material having adherent and non-adherent surface areas which comprises applying finely divided, solder wettable, metal or alloy particles to the surface areas; removing any excess metal or alloy particles from the non-adherent areas; the improvement comprising treating the particulate metallized areas with solder flux and subsequently with molten solder to form a soldered electrically conductive circuit.

A printed circuit element of the invention comprises, in order, (a) a substrate; (b) an imaged layer, at least about 0.00005 inch (0.0013 mm) in thickness, of an imaged photoadhesive composition having adherent and non-adherent surface areas; (c) finely divided, solder wettable, metal or alloy particles solely in the adherent image areas; and (d) a layer of solder adhered to the areas having the metal or alloy particles.

The printed circuit substrates employed in the present invention can be any one of the various kinds of sheets, plates, synthetic resin plates, synthetic resin laminated plates or composites, etc., having the

necessary electrical and mechanical properties, chemical resistance, heat resistance, etc. Examples of resins include: phenolformaldehyde, epoxy and melamine resins, etc. Glass plates, ceramic or ceramic coated metal plates are also useful. The substrate can also be a paper, cardboard, fiber, including glass cloth, wooden sheet material or paper base phenolic resin laminate. Paper base without resin is particularly useful in producing low cost printed circuits. Metal sheets, e.g., with holes, can be used provided that a material adhered thereto acts as a barrier between the metal sheet support and the built-up metallized circuit. Also useful are self-supported photohardenable elements as disclosed in U. S. Patent 4,054,479.

A material that is adherent or tacky or capable of being made adherent by a suitable treatment, e.g., heating or chemical treatment, is applied in the form of a liquid or a solid layer to the surface of the substrate or circuit board. One type of adherent material that is useful is an adhesive which may be painted on the circuit board in the form of the desired electrical circuit. Silk screen printing techniques such as are described in Printed Circuits Handbook, C. F. Coombs, Jr., Editor, McGraw-Hill, Inc., New York, New York, 1967, pages 4-25 to 4-37 are other means of applying adherent materials. Generally, in screen printing an ink is prepared in which suitable printing adaptability is imparted to the adhesive. The adhesive may be an epoxy resin, phenol resin, rubber phenol or polyvinyl butyral and may contain a filler such as a pigment, e.g., carbon, TiO_2, zinc oxide, etc. U. S. Patents 3,391,455 and 3,506,482 disclose adhesives that have excellent adhesive force, electrical properties and high resistance to heat and chemicals and describe methods of application of the adhesives to circuit boards. Suitable thicknesses for the adhesive ink is about 20 to 50 microns.

A preferred type of adherent material is a photoadhesive composition such as a photohardenable, photosoluble, or photodesensitizable composition in liquid form, e.g., solution, suspension, etc., which can be applied to a circuit board by conventional means, e.g., dip coating, spin coating, coating with a doctor knife, spraying, etc. or in the form of a dry layer. For the purposes of this invention a photoadhesive composition is a photosensitive composition which upon imagewise exposure to actinic light will form adherent image areas in either exposed or unexposed image areas either directly or after subsequent treatment of the composition. The photohardenable composition includes photopolymerizable layers capable of addition polymerization, photocrosslinkable layers, and photodimerizable layers. Many specific examples of such photohardenable layers are set forth in the following U. S. Patents which are incorporated herein by reference: 3,469,982; 3,526,504; 3,547,730; 3,060,024; 3,622,334; 3,649,268; and French Patent 72 11658. The photosoluble compositions disclosed in U. S. Patent 3,837,860 and the photodesensitizable compositions disclosed in U. S. Patent 3,778,270 are also useful.

A preferred element contains a photohardenable image-yielding stratum on a strippable support. The photohardenable composition is generally present in a dry coating thickness of about 0.00005 to about 0.10 inch (0.0013 to 2.54 mm) or more and preferably about 0.0003 inch (~0.0008 cm) to about 0.01 inch (~0.025 cm). A removable cover sheet may be present over the photohardenable layer. Photohardenable, e.g., photopolymerizable, layers and elements are more fully described in U. S. Patent 4,054,483, the disclosure of which is incorporated by reference.

Photopolymerizable compositions generally contain at least one binder, ethylenically unsaturated monomers, initiators or initiator system, thermal polymerization inhibitors and other additives such as dyes, pigments, plasticizers, etc.

Once a photosensitive composition or layer is applied to the printed circuit substrate, it is exposed imagewise and either directly forms or can be rendered to form adherent and non-adherent image areas. Suitable radiation sources depend on the photosensitive composition type. Generally, however, radiation sources that are rich in ultraviolet radiation are useful. Radiation sources are disclosed in U. S. Patents 2,760,863 and 3,649,268. The exposure may be through a phototool, negative or positive, having the circuit image including circuit trace.

Solder wettable metal and alloy particles or combinations thereof are applied to the adherent and non-adherent image areas to produce particulate, metallized, adherent image areas. Suitable particles include: copper, and copper alloys, e.g., copper-tin alloy; tin-lead alloy; aluminum; gold; silver; nickel and nickel alloys; lead and tin that are solder wettable. Also useful are metal coated particles, e.g., silver-coated glass. Copper powder is preferred because of its high conductivity and low cost. The particles have an average diameter of about 0.5 to 250 microns, 5 to 20 microns in average diameter being a preferred particle size. Mixed particle sizes can be used including larger sized particles followed by smaller particles. A more preferred average particle diameter is 8 to 11 microns.

The particles can be applied by known methods, including, but not limited to, the toning methods described in the patents listed in the "Background Art" section and U. S. Patents 3,391,455

and 3,506,482. Another useful application technique is by use of a fluidized bed of particles, Research Disclosure, June 1977, No. 15882 by Peiffer and Woodruff. It is important that any excess metal or alloy particles which may be present be removed from the non-adherent or non-tacky image areas. In some embodiments, excess particles are not present or, if present, may be removed during the soldering operation. Suitable mechanical and other means for removing excess particles are described in the above-mentioned U. S. patents and Research Disclosure.

Although a short heating period is preferred to rapidly improve adhesion of metal particles to the adherent image surfaces, other methods may be used. In some instances, the substrate with the particulate metallized image thereon may simply be held at room temperature for a period of time, e.g., overnight, or pressure may be applied to the particulate image. In other instances, the imaged photoadhesive material may be treated with a volatile solvent or plasticizer for adherent image areas either before, during or after the solder-wettable metal particles are applied. When photoadhesion is improved by such liquid treatment further curing or hardening steps may not be necessary as exemplified in Example 11 below. Preferably, however, the particulate metallized areas are subsequently hardened or cured by heating, by exposing to actinic radiation, by treating with a suitable hardening or curing catalyst or reagent or other such methods known to those skilled in the art. While the preferred hardening or curing step generally precedes application of molten solder, the hardening or curing reaction in some instances may be combined with and occur concurrently with the soldering operation. Heating can be carried out by baking, e.g., at about 170°C. or less,

or by such radiative heating from infrared or microwave sources. The heating temperature must be below the degradation temperature of the adherent composition. The curing or hardening may be accelerated by prior treatment with a suitable catalyst or reagent which may be present on the metal particles or in the solder flux or may be applied independently. When the metallized material or area is photohardenable, it may be hardened by uniform exposure of the metallized element to actinic radiation preferably after a short heating period, e.g., 10 to 100 seconds at about 150° to 180°C., as exemplified in Example 4. The hardening step is dependent on many variables such as the composition used to form the adherent image and its reactivity to heat, light or reagents, the thickness of the applied composition, the mode and conditions of applying hardening energy, etc.

Prior to soldering, the metallized areas are treated by known procedures with solder fluxes typified by the following compositions:

Rosin type, organic, e.g., a mixture of diterpene acids in alcohol, water, or other appropriate solvent;

Inorganic acids, e.g., HCl, orthophosphoric acid, etc.;

Inorganic salts, e.g., zinc chloride, ammonium chloride and combinations thereof used to produce HCl upon heating in the presence of water;

Organic acids, e.g., lactic, citric, oleic, etc.;

Organic halogen compounds, e.g., aniline hydrochloride, etc.;

Organic amines and amides, e.g., urea, etc.

As indicated above, these fluxes can contain curing or hardening catalysts or reagents.

The fluxed image areas are subsequently exposed to molten solder, e.g., solder waves, etc. Known solder compositions can be used, e.g., tin, lead combinations, and compositions containing bismuth, cadmium, indium, silver and antimony. When the adherent material is thermally stable, low melting metals alone may be used, e.g., tin, lead, indium, etc. Preferred solders particularly useful in the preparation of printed circuits are tin/lead in ratios of 63/37 and 60/40. It is important to balance the ability to solder with the adhesion of the metal particles in the adherent image areas, e.g., the areas should be tacky enough to adhere the metal particles but not too tacky whereby the particles would become coated or engulfed with the tacky material.

Best Mode For Carrying Out The Invention

The best mode for carrying out the invention is as follows: A film supported photopolymerizable layer as described in Example 4 is laminated to a glass-epoxy based printed circuit board also as described in Example 4. The photopolymerizable layer is exposed through a photographic positive circuit pattern for 10 seconds to the ultraviolet radiation source described in Example 1. After removing the support, copper powder, 8 microns in average diameter, is applied in a fluidized bed. The board is heated for 30 seconds at 160°C. (external reading), and the excess copper is removed by brushing. The metallized board is passed through the ultraviolet exposure source described in Example 4. The circuit pattern is brushed with an aqueous solder flux as described in Example 5 and is soldered as described in that Example at 16 feet/minute (48.77 m/minute). A highly conductive printed circuit element is obtained.

Industrial Applicability

The process of this invention is easily adapted to automation and is applicable to the preparation of fine conductive wiring traces, and low cost printed circuits. The process is also useful in preparing multilayer circuits by using previously prepared printed circuits as the substrate in the process of this invention as described above and/or repeating the operations of the process with additional layers of photoadhesive material adhered to each successive underlying printed circuit and exposing in register with an appropriate phototool for the successive layer. Through-holes can be introduced at appropriate junctures to permit electrical connecting between layers and/or allow insertion of electrical components to be soldered into the finished boards. Through-holes may be introduced into the boards by conventional methods used in fabricating multilayer printed circuits. Stepwise, a procedure for preparing multilayer circuits is as follows:

(1) applying a photoadhesive layer to a previously prepared printed circuit board,

(2) exposing the photoadhesive layer to actinic radiation through an appropriate phototool in register with the underlying printed circuit,

(3) applying finely divided solder wettable metal or alloy particles to the adherent image areas,

(4) removing any excess metal or alloy particles from the non-adherent image areas, and

(5) treating the particulate metallized surface with solder flux and subsequently with molten solder to obtain a two-layer multilayer circuit.

Additional circuit layers are added by repeating steps (1) through (5) using an appropriate phototool in register with at least one of the

underlying printed circuits in each step (2). Similarly double-sided multilayer circuit boards may be produced by carrying out steps (1) through (5) one or more times on each side of a previously prepared double-sided printed circuit board.

If interconnections are desired between two or more of the layers, the soldered circuit of step (5) above can be further processed as follows:

(6) drilling or punching holes in the desired junction areas of the board;

(7) catalyzing the holes with a conventional solution of tin and palladium chlorides;

(8) cleaning the board to remove the catalyst from the board side surfaces; and

(9) electrolessly plating the conductive through-holes with metal to complete the electrical interconnections.

When the photoadhesive material is a photopolymerizable material or other oxygen-sensitive material, the imaging exposure may be carried out in an inert atmosphere, e.g., nitrogen, or the surface of the photoadhesive layer may be laminated with an oxygen-impermeable film cover sheet, e.g., polyester film, or may be coated with a layer that functions as a barrier to oxygen. In the instance when a film or barrier coating is used, the film or coating is removed before application of the finely divided particulate metal particles.

In the preferred process each particulate metallized layer is hardened or cured either before or during the soldering step (5) as previously described.

The photoadhesive material may be applied by either laminating a film element directly to the previously prepared circuit board or the board may be

coated with a solution of the material and dried. Such a laminating procedure may be by a process analogous to Example 4 of U. S. Patent 4,054,483 wherein direct soldering of metallized powder images would replace electroless plating.

The coating procedure is also useful in preparing multilayer circuits which are connected by through-holes. The preparation of such multilayer circuits is illustrated by Example 2. Stepwise, such a procedure for preparing multilayer circuits is as follows:

1. holes are drilled or punched in a previously double-sided printed circuit board with or without plated through-holes;

2. the board, including hole walls, is coated with a solution or suspension of photopolymer composition;

3. each board side is laminated with a film cover sheet, e.g., polyester film, or is coated with a solution that functions as a barrier to oxygen;

4. each side of the board is exposed to actinic radiation through an appropriate phototool;

5. each cover sheet or oxygen barrier layer is removed;

6. solder wettable metal powder, e.g., copper, is applied to the adherent unexposed image areas on both sides of the circuit board as well as to the hole walls;

7. the particulate metallized areas are hardened or cured by heating or uniformly exposing to actinic radiation; and

8. each metallized surface and through-holes are treated with solder flux and subsequently with molten solder to obtain a four-level multilayer circuit in which the two outerlayers are interconnected.

The prepared circuits of this invention can be covered with a solder mask composition and preferably a photosensitive flame retardant solder mask film. Subsequently, an adherent image can be made over the solder mask, and a circuit of the image can be made using the process of this invention. In some instances where the solder mask is photosensitive, the solder mask itself may be used to form an adherent image. An adherent image on either side of the prepared circuit may also be used to add visible nomenclature and/or graphics by toning adherent image areas with suitable pigments. Useful toning procedures and elements are described in U. S. Patent 3,060,024; 3,620,726 and 3,649,268.

Examples

The invention will be illustrated by the following examples wherein the parts and percentages are by weight.

Example 1

A photopolymerizable composition containing the following ingredients:

copolymer of methyl methacrylate (46%), acrylonitrile (9%), butadiene (14%), and styrene (31%)	1,505 g.
solid unsaturated urethane resin (M.W. ca. 1,900; 0.5% unsaturation)	1,505 g.
trimethylol propane triacrylate	705 g.
triethylene glycol diacrylate	705 g.
benzophene	140 g.
4,4'-bis(dimethylamino)-benzophenone	140 g.
methylene chloride	8,770 g.

is coated on a 0.025 mm thick polyethylene terephthalate support, and the layer is dried to a

thickness of about 0.038 to 0.51 mm. The photopolymerizable layer is laminated to a glass-epoxy base printed circuit board, and the photopolymerizable layer is exposed for 20 seconds through a photographic positive pattern to ultraviolet radiation of a 400 watt, medium pressure, mercury vapor lamp in a Model DMVL Double Sided Exposure Frame, a product of Colight, Inc., Minneapolis, Minn. The polyethylene terephthalate support is removed, and the photopolymerized surface is dusted with copper powder, less than 35 microns to more than 150 microns in average diameter, Fisher copper metal C-434 marketed by Fisher Scientific Co., Fair Lawn, New Jersey. The excess powder is removed in the exposed non-tacky areas with a fine water spray leaving a circuit pattern defined by the adherent copper powder. The metallized laminate is baked for 1 hour at 160° to 165°C. and is brushed with a rosin type solder flux, Alpha® 809, manufactured by Alpha Metals, Inc., Jersey City, New Jersey. The fluxed laminate is passed over a solder wave, tin/lead (60/40), in a Model 201396 Wave Soldering Machine manufactured by Hollis Engineering, Inc., Nashua, New Hampshire. The solder adheres only to those regions where the copper powder is adherent to form a conductive printed circuit.

<u>Example 2</u>

Printed circuits are prepared on each side of two printed circuit boards as described in Example 1. Holes are drilled in the circuit boards and the boards, including the hole walls, are coated with the following photopolymer solution:

	Parts
Copolymer of methyl methacrylate (46%), acrylonitrile (9%), butadiene (14%), and styrene (31%)	33
Trimethylol propane triacrylate	16
2-tert-butyl anthraquinone	1
Toluene	77
Methylene chloride	118

To each side of the coated circuit boards is laminated a polyethylene terephthalate film, 0.025 mm in thickness. Each side of the circuit boards is exposed for 60 seconds to the ultraviolet radiation source described in Example 1 through a circuit image. The polyethylene terephthalate films are removed and copper powder, 11 microns in average diameter, Alcan® MD 183 manufactured by Alcan Metal Powders, division of Alcan Aluminum Corp., Elizabeth, New Jersey, is applied to the unexposed regions on both sides and to the walls of the holes in each board and the excess copper powder is removed. The metallized circuit boards are baked for one hour at 160°-165°C. The metallized areas including holes are brushed with the solder flux described in Example 1 and then are soldered using the solder and procedure described in Example 1. Two four-level multilayer circuits in which the two outer layers are interconnected are obtained.

Holes are drilled in one of the multilayer circuit boards. The holes are catalyzed with a solution of tin and palladium chlorides and the board is washed with water to remove catalyst from both sides of the board. The board is electroless copper plated as described below to obtain conductive through-holes interconnecting the four circuit layers.

The prepared board is dipped for 30 seconds in a 20% by weight solution of sulfuric acid and then placed for 16 hours in an electroless copper plating bath, HiD-410 manufactured by Photocircuits Division, Kollmorgen Corp., Glen Cove, Long Island, New York.

The plating on the original printed circuit trace is good.

Example 3

On an insulating base phenolic resin laminate, an electrically conductive circuit trace is printed by a silk-screen printing process using an adhesive composition. The adhesive composition is prepared by adding to 30 g. of epoxy resin consisting of Achmex® R-11 and 10 g. of Achmex® H-85 3 g. of carbon. Copper powder, 8 to 11 microns in average diameter, is dusted onto the layer of the adhesive to completely cover the adhesive print. A pressure of 0.5 to 1.0 g/cm.^{2} is applied thereon to have copper particles secured to the adhesive. The copper particles not secured to the adhesive are removed, and the adhesive is cured by heating at 150° ± 10°C. for about 1 hour. The metallized image is brushed with the solder flux described in Example 1 and passed over a solder wave, tin/lead (63/37), using the Wave Soldering Machine described in Example 1. The solder adheres only to those regions where the copper powder is adherent to form a conductive printed circuit.

Example 4

A film supported photopolymerizable layer, 3 mils (~0.08 mm) in thickness, of the following composition:

	Parts
Pentaerythritol triacrylate	25.0
Di-(2-acryloxyethyl) ether of tetrabromo Bisphenol-A	10.0
Di-(3-acryloxy-2-hydroxy-propyl) ether of Bisphenol-A	15.0
Methyl methacrylate(46)/acrylo-nitrile(9)/butadiene(14)/styrene(31) copolymer	30.0
Methyl methacrylate(95)/ethyl methacrylate(5) copolymer	8.0
Michler's ketone	0.4
Benzophenone	5.3
Antimony oxide (Sb_2O_3)	6.0
Monastral Green pigment	0.3

is laminated at 105°C. to a glass-epoxy base printed circuit board 31 mils (~0.79 mm) thick, and the polymerizable layer is exposed for 30 seconds through a photographic positive pattern and the support to ultraviolet radiation from the radiation source described in Example 1. The support is removed and the polymerized surface is dusted with copper powder, about 35 to 150 microns in average diameter, Fisher copper metal C-434, marketed by Fisher Scientific Company, Fair Lawn, New Jersey. The excess powder is removed by shaking the dusted board, and the board is heated for 1 minute at 160°C. The dusted circuit board is passed twice through a CTF Laminator, Model 1200, manufactured by E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware. The circuit pattern defined by the adhered copper powder is dusted with copper powder, 11 microns in average diameter, Alcan® MD-183 manufactured by Alcan Metal Powders division of Alcan Aluminum, Elizabeth, New Jersey. The excess copper powder is removed by shaking the dusted board, and the dusted

board is heated for 1 minute at 160°C. The metallized board is passed twice through an ultraviolet exposure source at 10 ft./minute (3.05 m/minute), Model PC-7100 UV Processor, manufactured by Argus International, Hopewell, New Jersey to harden the photopolymer matrix. The circuit pattern defined by the adhered large and small copper powder is brushed with an aqueous solder flux, Alpha® 709-F, manufactured by Alpha Metals, Inc., Jersey City, New Jersey and then is passed over a solder wave in the wave soldering machine described in Example 1. A conductive solder printed circuit is obtained on the original printed circuit trace.

Example 5

A film supported photopolymerizable layer, as described in Example 4, is laminated to a glass-epoxy based printed circuit board also as described in Example 4. The photopolymerizable layer is exposed for 20 seconds through a photographic positive radio circuit pattern and the support to ultraviolet radiation from the radiation source described in Example 1. The support is removed and the polymerized surface is dusted with copper powder, about 11 microns in average diameter, as described in Example 2. The copper powder adheres to the unexposed image areas. The excess powder is removed by shaking the dusted board, and the board is heated for 30 seconds at 160°C. (external reading). The metallized board is passed once through an ultraviolet exposure source as described in Example 4. The circuit pattern defined by the adherent copper powder is brushed with an aqueous solder flux, Alpha® 709-F, manufactured by Alpha Metals, Inc., Jersey City, New Jersey and then soldered with tin/lead (60/40) at 6 feet/minute (1.83 m/minute) using a wave solder unit manufactured by Hollis Engineering, Inc., Nashua, New Hampshire. Through holes are drilled in the board

and components soldered to it. The radio works without problems.

Example 6

Example 5 is repeated with the following variations: the glass-epoxy based printed circuit board is replaced by a 0.062 inch (1.57 mm) thick paper base phenolic resin laminate, the surface of which is roughened. The lamination of the photopolymerizable layer is accomplished at 115°C. in a vacuum laminator, Riston® A-1 Vacuum Laminator manufactured by E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware. Copper powder, about 8 microns in average diameter, Alcan® MD-301 manufactured by Alcan Metal Powders division of Alcan Aluminum, Elizabeth, New Jersey, is applied in a fluidized bed. After the excess copper powder is removed, the metallized board is heated for 50 seconds at 160°C. The radio works satisfactorily without problems.

Example 7

Example 6 is repeated except that a 10-ply cardboard Beveridge Paper Co., division Scott Paper, Indianapolis, Indiana, is used as the base circuit board, which is baked at 140°C. for 1.5 hours and is vacuum laminated on both sides at 115°C. with the photopolymerizable layer. The second side is entirely exposed. Resistance for a 0.1 inch (2.54 mm) wide soldered line for its length is zero, or equal to copper.

Example 8

A 0.031 inch (~0.79 mm) piece of pressboard (grey cardboard) is dipped for 30 seconds into a methylene chloride solution (20% solids) of the photopolymerizable composition described in Example 4 except that no pigment is present. The dipped self-supported board is air dried for 1 hour, is heated for

30 seconds in an infrared heater and is left in the open air at room temperature for two hours. After a polyethylene terephthalate film, 0.025 mm in thickness, is vacuum laminated to each surface, each side of the board is exposed through the laminated film to a positive circuit pattern for 30 seconds in the exposure source described in Example 1. Each laminated film is removed, and the exposed board is toned in a fluidized bed using the copper powder as described in Example 6. Excess copper powder is removed, the metallized board is heated and then is passed through an ultraviolet exposure source as described in Example 4 to expose each side. The circuit patterns defined by the adherent copper powder are fluxed as described in Example 5 and soldered by dipping in a tin/lead (60/40) solder mixture. Satisfactory soldered circuits are obtained.

<u>Example 9</u>

A 0.031 inch (~0.79 mm) piece of sheet steel is cleaned in a Model SBC-12F circuit board cleaning machine (Somaca®) and after drying is laminated with a film-supported photopolymerizable layer described in Example 4. The photopolymerizable layer is exposed for 15 seconds through a photographic positive pattern and the support to ultraviolet radiation from the radiation source described in Example 1. The film support is removed and copper powder is applied to the imaged layer as described in Example 6. The metallized board is heated for 30 seconds at about 150°C., cooled, and then brushed to remove excess copper. The metallized board is passed once through the ultraviolet exposure source as described in Example 4; the circuit pattern defined by the copper powder is brushed with an aqueous solder flux as described in Example 4, and then is passed over a solder wave tin/lead (63/37), using the

wave soldering machine described in Example 1. The solder adheres only to those regions where the copper powder is adherent to form a circuit in which resistance between non-connected lines is greater than 2 X 10^6 ohms.

Example 10

A film supported photopolymerizable layer, as described in Example 4, is laminated to a glass-epoxy based printed circuit board also as described in Example 4. The photopolymerizable layer is exposed for 30 seconds through a photographic positive circuit pattern and the support to ultraviolet radiation from the radiation source described in Example 1. The support is removed and the polymerized surface is dusted with copper powder, about 11 microns in average diameter, as described in Example 2. The copper powder adheres to the unexposed image areas. The excess powder is removed by shaking the dusted board, and the board is allowed to stand for 24 hours at room temperature. The metallized board is passed twice through an ultraviolet exposure source as described in Example 4. The circuit pattern defined by the adherent copper powder is brushed with a rosin-type solder flux as described in Example 1 and is then soldered with tin/lead (60/40) at 6 feet/minute (1.83 mm/minute) using a wave solder unit manufactured by Hollis Engineering, Inc., Nashua, New Hampshire.

Example 11

A photopolymerizable element comprising a 0.01 inch (0.25 mm) thick metal support, an 0.018 inch (0.46 mm) thick cellulosic photopolymerizable layer, and a polyethylene terephthalate cover sheet is prepared, the cellulosic layer having the following composition:

	Parts
Cellulose hydroacetate	36.0
Cellulose acetate	9.0
Triethylene glycol diacrylate	24.1
Succinic anhydride	13.8
Tributoxyethyl phosphate	13.0
Glutaric acid	1.0
2-ethylanthraquinone	0.1
Methyl ethyl hydroquinone	0.18
Diethylcyclohexyl amine	3.0

The element is exposed through the cover sheet to a positive circuit image for 30 seconds by means of the exposure source described in Example 1. The cover sheet is removed, and the exposed element is dipped into ethyl Cellosolve® (2-ethoxy ethanol), and the element is wiped to remove excess liquid. Copper powder, about 8 microns in average diameter, is applied as described in Example 6, and the excess copper powder is removed by brushing. After setting overnight, the circuit lines are fluxed with 5% by volume HCl, are wiped dry, and are wave soldered as described in Example 5. Lines of 0.10 inch (2.54 mm) and 0.02 inch (0.51 mm) are found to be highly conductive.

Claims

1. In a process for producing a printed circuit containing an electrically conductive circuit trace from a material having adherent and non-adherent surface areas which comprises applying finely divided, solder wettable, metal or alloy particles to the surface areas; removing any excess metal or alloy particles from the non-adherent areas; the improvement comprising treating the particulate metallized areas with solder flux and subsequently with molten solder to form a soldered electrically conductive circuit.

2. A process according to Claim 1 wherein the particulate metallized areas are hardened or cured prior to or during treatment with molten solder.

3. A process according to Claim 2 wherein the particulate metallized areas are hardened or cured by heating, by exposing to actinic radiation or by treating with a hardening or curing reagent.

4. A process according to Claim 1 wherein the particulate metallized areas are heated to less than 180°C. before treatment with molten solder.

5. A process according to Claim 1 wherein the finely divided, solder wettable, metal or alloy particles have an average diameter of about 0.5 to about 250 microns.

6. A process according to Claim 1 wherein the metal particles are copper or a copper alloy.

7. A process according to Claim 1 wherein the adherent and non-adherent surface areas are tacky and non-tacky surface areas, respectively, and are present in an imaged layer of photoadhesive composition.

8. A process according to Claim 7 wherein the photoadhesive composition is a photohardenable composition taken from the group consisting of photopolymerizable, photocrosslinkable, and photodimerizable compositions.

9. In a process for producing a printed circuit containing an electrically conductive circuit trace from a circuit board substrate bearing a layer of a photohardened composition having adherent and non-adherent surface areas which comprises applying copper particles, 5 to 20 microns in average diameter, removing excess copper particles from the non-adherent areas, heating the circuit board; the improvement comprising treating the particulate metallized areas with solder flux and subsequently with molten solder to form a soldered electrically conductive circuit.

10. A process according to Claim 9 wherein the circuit board is heated to less than 180°C. for less than 100 seconds.

11. A process according to Claim 9 wherein the adherent areas containing copper particles are hardened by heating, by exposing to actinic radiation or by treating with a hardening or curing reagent either prior to or during treatment with molten solder.

12. A process according to Claim 9 wherein the areas are hardened by exposing uniformly to actinic radiation prior to treatment with molten solder.

13. A process for making a multilayer printed circuit board according to Claim 9 wherein the circuit board substrate contains thereon a previously prepared printed circuit.

14. A process according to Claim 1 wherein a multilayer printed circuit element is prepared comprising

1) applying a photoadhesive layer to a previously prepared printed circuit board,
2) exposing the photoadhesive layer to actinic radiation through an appropriate phototool in register with the underlying printed circuit,
3) applying to the adherent image areas finely divided, solder wettable metal or alloy particles,
4) removing any excess metal or alloy particles from the non-adherent image areas,
5) treating the particulate metallized surface areas with solder flux and subsequently with molten solder to obtain a two-layer multilayer circuit.

15. A process according to Claim 14 wherein multilayer printed circuit elements having three or more circuit layers are prepared by repeating at least once steps 1) through 5) for each additional circuit layer using the multilayer circuit previously prepared in each subsequent step 1) and using the appropriate phototool in register with at least one of the underlying printed circuits in each step 2).

16. A process according to Claim 14 wherein holes are drilled or punched in desired junction areas of the soldered electrically conductive, multilayer printed circuit board; the holes are catalyzed with a colloidal suspension of stannous and palladium

chlorides; the circuit board is cleaned to remove excess catalyst from the board side surfaces; and electroless metal plate is applied to obtain electrically conductive through holes interconnecting the multi-layered printed circuit.

17. A process according to Claim 1 wherein a printed circuit containing an electrically conductive circuit trace is present on each side of a circuit board material; holes are drilled or punched in the circuit board; a photohardenable composition is applied to the surface of the circuit board and hole walls; a cover sheet is laminated to each side of the circuit board; each side of the circuit board is exposed through an image-bearing transparency to actinic radiation for the photohardenable layer; the cover sheets are removed; solder wettable metal or alloy particles, 5 to 20 microns in average diameter, are applied to the exposed surface and hole walls; the metallized printed circuit is heated, and the metallized areas and holes are treated with solder flux and subsequently with molten solder to form a soldered electrically conductive multilayer printed circuit.

18. A printed circuit element which comprises, in order,

(a) a substrate;

(b) an imaged layer, at least about 0.00005 inch (0.0013 mm) in thickness, of an imaged photoadhesive composition having adherent and non-adherent surface areas;

(c) finely divided, solder wettable, metal or alloy particles solely in the adherent image areas; and

(d) a layer of solder adhered to the areas having the metal or alloy particles.

19. An element according to Claim 18 wherein the substrate is paper.

20. An element according to Claim 18 wherein the substrate is a paper base phenolic resin laminate.

21. An element according to Claim 18 wherein the substrate is a glass cloth reinforced with epoxy resin.

22. An element according to Claim 18 wherein the substrate is metal.

23. An element according to Claim 18 wherein the solder wettable particles are copper or a copper alloy.

24. An element according to Claim 23 wherein the solder is a tin, lead combination.

25. An element according to Claim 18 wherein the solder wettable particles have an average diameter of about 0.5 to about 250 microns.

26. An element according to Claim 18 wherein the photoadhesive composition is a photohardenable composition taken from the group consisting of photopolymerizable, photocrosslinkable, and photodimerizable compositions.

27. An element according to Claim 26 wherein the photohardenable composition is a flame retardant photopolymerizable composition.

28.. An element according to Claim 18 wherein the photoadhesive is hardened or cured.

29. An element according to Claim 18 having one or more successive layers of (b), (c) and (d).

30. A printed circuit element according to Claim 18 having electrical components inserted in said element.

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EUROPEAN SEARCH REPORT

Application number

EP 79 10 0263

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	NL - A - 278 021 (KODAK-PATHE) * Page 3, line 9 - page 7, line 9; claims * --	1,6,7 9,14, 23	H 05 K 3/24 3/10 3/18 3/00 G 03 C 5/00
D	US - A - 3 506 482 (MATSUSHITA) * Column 2, line 4 - column 4, line 62; claims, figures * --	1-7,9-11,14 16,18 20,23 25,28	
	GB - A - 1 429 082 (NITTO ELECTRIC INDUSTRIAL CO. LTD.) * Page 1, line 80 - page 5, line 64; page 6, line 117 - page 7, line 7; claims * ----	1,6-9	TECHNICAL FIELDS SEARCHED (Int.Cl.³) H 05 K 3/24 3/34 3/10 3/18 3/00 G 03 C 5/00 G 03 F 7/20

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	14-05-1979	GORUN

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